STRUCTURAL EFFECTS IN NON-ELECTROLYTE SOLUTIONS

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ABSTRACT. Non-polar central forces and non-central forces of both weak dipolar and of structural origin have been combined into a single potential. Neglecting higher order terms the excess thermodynamic functions of a mixture of non-polar globular molecules with weakly polar globular molecules have been found to consist of four terms : pure non-polar, pure dipolar, polarisabilities and structural, g^E, h^E and v^E have been predicted for the systems fluorobenzene-carbon tetrachloride, fluorobenzene-benzene and fluorobenzene-cyclohexane for which experimental data exist. Agreement between predicted and experimental values are satisfactory for all the systems.

INTRODUCTION

Anantaraman Bhattacharyya, and Palit (1961, 1962, 1963) recently discussed the thermodynamics of liquid mixtures the molecules of both components being spherical but those of one of the components also having a point dipole at the centre. Balescu's theory [Balesce (1955), Prigogine (1957)] was modified and used to predict the excess functions with considerable success. It seemed however that the description of a molecule like chloro- or fluorobenzene as a spherical polar molecule was not quite correct; some discrepancies, particularly for the systems like fluorobenzene-benzene and fluorobenzene-carbon tetrachloride appeared to be due to the presence of another effect. It was suggested that this may have originated from the non-spherical nature of the component molecules. Carbon tetrachloride and benzene are not strictly spherical and it would be more realistic to describe a molecule like fluorobenzene as a globular molecule with a point dipole at the centre.

The object of this work is to develop a simple potential for such a molecule which will permit a calculation of the effects of the different contributions to the molecular interactions.

Various treatments of the potential have combined non-polar central forces with non-central forces. These latter have either been assumed due to weak dipoles or due to a molecular strueture which lacks spherical symmetry [Rowlinson, et al (1955), Prigogine (1957)]. In this work we attempt to synthesize the two approaches and arrive at the desired potential.

According to Rowlinson et al (1955) the potential for a globular molecule is obtained from a Lennard Jones potential of spherical symmetry through the perturbation of the attractive term alone by a small non-central term.

$$\epsilon(r) = \epsilon^0[(r^0/r)^{12} - 2(r^0/r)^6\{1 + \alpha g(\theta_1, \theta_2, \theta_{12})\}] \tag{1}$$

where α is a small parameter and g is a sum of products of surface harmonics. Taking an average over the angles this gives rise to a temperature dependent parameter $\delta(T)$ which is proportional to the square of the coefficients of the non-central terms of globular origin.

$$\delta_{ij}(T) = \frac{\epsilon_{ij}\alpha_{ij} < g_{ij}(\omega) >}{kT} \tag{2}$$

$< g_{ij}(\omega) >$ denotes an unweighted average over all angles. The essential simplifications made by them to arrive at this simple form of potential are; (1) neglect of potentials which lead to triplet terms, (2) neglect of variation of repulsive forces, (3) assumption of $a\,(n, n/2)$ potential for the central forces which lead to a hypothetical potential conformal with the original unperturbed potential but which is a function of temperature. This hypothetical potential has the form

$$\begin{aligned} \epsilon(r) &= \epsilon^*[(r^*/r)^{12} - 2(r^*/r)^6] \\ &= \epsilon^0[(r^0/r)^{12}\{1 - 2\delta(T)\} - 2(r^*/r)^6] \end{aligned} \tag{3}$$

According to Prigogine (1957) such a procedure is rather arbitrary when applied to globular molecules. Non-central forces should decrease more rapidly with increasing distance than forces of spherical symmetry, a fact which does not appear in (3). g is not specified and (2) is not explicit and can only be used empirically to fit certain experimental data.

In spite of this criticism of Prigogine the hypothetical potential seems to be useful owing to its simplicity in form and the author and his colleagues have been able to predict the thermodynamic functions of mixtures of non-polar polyatomic molecules with some success. One can now take advantage of the r^{-6} dependence of the attractive part of this potential and introduce a point-dipole at the centre of such a molecule similar to what has been done by Balescu (1957) to a strictly spherical molecule. We can write down the potential as follows :

$$\epsilon(r) = \epsilon^0[(r^0/r)^{12}(1 - 2\delta) - 2(r^0/r)^6] + \bar{\epsilon}_d \tag{4}$$

where $\bar{\epsilon}_d$ is the average value of the dipolar interaction over all orientations, $\bar{\epsilon}_d$ being

$$\bar{\epsilon}_d = -\frac{1}{3kT} \cdot \frac{\mu^4}{r^6} - \frac{2\mu^2\alpha}{r^6} \tag{5}$$

For a like pair of molecules the potential now becomes

$$\epsilon(r) = \epsilon^0 \left[(r^0/r)^{12}(1-2\delta) - 2(r^0/r)^6 \left[1 + \frac{1}{6} \left(\frac{\bar{\mu}^4}{\bar{T}^0} + \bar{\alpha}\bar{\mu}^2 \right) \right] \right]$$

$$= \epsilon^*[(r^*/r)^{12} - 2(r^*/r)^6] \qquad \ldots (6)$$

where the reduced parameters $\bar{\mu}$, $\bar{\alpha}$ and $\bar{T}^0$ are defined by

$$\bar{\mu} = \frac{\mu}{(\epsilon^0 r^{03})^{\frac{1}{2}}} \; ; \; \bar{\alpha} = \frac{\alpha}{r^{03}} \; ; \; \bar{T}^0 = \frac{kT}{\epsilon^0}$$

Equation (6) shows that this potential is also conformal with the original unperturbed potential but dependent on temperature. The characteristic molecular parameters ϵ^* and r^* of this new potential are related to the unperturbed ϵ^0 and r^0 as below

$$\epsilon^* = \epsilon^0 \left[1 + \frac{1}{3}\Gamma + 2\gamma + 2\delta + 2\delta \left(\frac{1}{3}\Gamma + 2\gamma \right) + \ldots \right]$$

$$= \epsilon^0[1+\psi(T)]$$

$$r^* = r^0 \left[1 - \frac{1}{36}\Gamma - \frac{1}{6}\gamma - \frac{1}{3}\delta + \frac{1}{6}\delta \left(\frac{1}{3}\Gamma + 2\gamma \right) + \ldots \right]$$

$$= r^0[1+\phi(T)] \qquad \ldots (7)$$

where $\Gamma = \dfrac{\bar{\mu}^4}{\bar{T}^0}$, $\gamma = \bar{\alpha}\,\bar{\mu}^2$

The production term $2\delta(\frac{1}{3}\Gamma + 2\gamma)$ contributes very little to the total perturbation and can safely be neglected for the present analysis. According to the general ideas of average potential theory eqn. (7) can be written down as

$$<\epsilon_i^*> = <\epsilon^0>(1+<\psi_i(T)>)$$

$$<r_i^*> = <r^0>(1+<\phi_i(T)>) \qquad \ldots (8)$$

For the composition dependent average potential, the average perturbation $<\psi_i>$ and $<\phi_i>$ being exactly similar to those found out by Balescu (1957).

For a mixture of two polarisable globular molecules where the component 2 has a permanent dipole moment of magnitude μ_2, the perturbations are now

$$\psi_{11} = 2\delta_{11} \; ; \qquad \phi_{11} = -\frac{1}{3}\delta_{11}$$

$$\psi_{12} = 2\delta_{12}+\gamma_{12}\ ;\quad \phi_{12} = -\frac{1}{3}\delta_{12}-\frac{1}{12}\gamma_{12}$$

$$\psi_{22} = 2\delta_{22}+\frac{1}{3}\Gamma+2\gamma_{22}\ ;\quad \phi_{22} = -\frac{1}{3}\delta_{22}-\frac{1}{36}\Gamma-\frac{1}{6}\gamma_{22} \qquad \ldots\ (9)$$

Following the procedure as outlined by Balescu with the potential (6) and perturbations (9) it is found that any excess function z^E now splits into four terms

$$z^E = z_0^E+z_d^E+z_p^E+z_s^E \qquad \ldots\ (10)$$

z_0^E, z_d^E, z_p^E and z_s^E are contributions due to central forces, pure dipolar, polarisabilities and those due to non-spherical or globular nature of the molecules respectively One may take the expressions* due to Prigogine *et al.* (1957) for z_0^E. These are

$$\frac{g^E_0}{x_1x_2} = h_1(2\theta-9\rho^2)+\tfrac{1}{2}TC_{p1}(_1\delta^2-4\theta\delta x_2-4\theta^2x_1x_2)-\tfrac{1}{2}TC_{v1}[\theta(x_1-x_2)+\tfrac{1}{2}\delta]^2$$

$$-\frac{3}{2}RT\rho[\theta(x_1-x_2)+\tfrac{1}{2}\delta+3\rho] \qquad \ldots\ (11)$$

$$\frac{h^E_0}{x_1x_2} = (h_1-TC_{p1})(2\theta-9\rho^2)-\tfrac{1}{2}T^2\frac{dC_{p1}}{dT}(\delta^2-4\theta\delta x_2-4\theta^2x_1x_2)$$

$$+\tfrac{1}{2}T^2\frac{dC_{v1}}{dT}[\theta(x_1-x_2)+\tfrac{1}{2}\delta]^2 \qquad \ldots\ (12)$$

$$\frac{v^E_0}{x_1x_2} = \frac{3}{2}v_1\rho\left[\theta(x_1-x_2)+\tfrac{1}{2}\delta+\frac{11}{4}\rho\right]+T\frac{dv_1}{dT}(-2\theta-\delta^2+4\theta\delta x_2+4\theta^2x_1x_2$$

$$+9\rho^2+3\rho\delta-6\rho\theta x_2)+\tfrac{1}{2}T^2\frac{d^2v}{dT^2}(-\delta^2+4\theta\delta x_2+4\theta^2x_1x_2) \qquad \ldots\ (13)$$

For z_d^E the expressions due to Anantaraman ( ) may be taken who retain θ in the expressions of dipolar excess functions.

$$\frac{g_d^E}{x_1x_2} = \tfrac{1}{8}\Gamma\{-h_1(1+\delta-3\rho x_2)-TC_{p1}[\tfrac{1}{2}\delta(3-x_1)+x_2\theta]$$

$$+\tfrac{1}{4}RT[1-x_2(\tfrac{1}{2}\delta-\theta+3\rho)]\} \qquad \ldots\ (14)$$

$$\frac{h_d^E}{x_1x_2} = \tfrac{1}{8}\Gamma(-2h_1+TC_{p1}-\tfrac{1}{4}RT)[1-x_2(\tfrac{1}{2}\delta-\theta+3\rho)] \qquad \ldots\ (15)$$

* Possibly several minor typographical errors occurred in the printing of equation (10.7.8) of Prigogine (1957). See also McLure et al. (1965).

$$\frac{v_d^E}{x_1x_2} = \tfrac{1}{8}\Gamma\left\{\left\{\tfrac{1}{4}v_1+T\frac{dv_1}{dT}\right\}[1+\tfrac{3}{2}\rho(1+x_1)-\tfrac{1}{2}x_2(\delta-2\theta)]\right.$$

$$\left.-\tfrac{5}{4}T\frac{dv_1}{dT}\delta(1+\tfrac{1}{2}x_2)\right\} \quad \ldots \quad (16^{+})$$

From the definition of γ_{12}

$$\gamma_{12} = \frac{\alpha_1\mu_2^2}{r_{12}^{06}\epsilon_{12}^0} \quad \ldots \quad (17)$$

We may write

$$\gamma_{12} = \frac{\alpha_1}{\alpha_2}\cdot\frac{\alpha_2\mu_2^2}{[\tfrac{1}{2}(r_{11}^0+r_{22}^0)]^6[\epsilon_{11}^0\theta+\tfrac{1}{2}(\epsilon_{11}^0+\epsilon_{22}^0)]} \quad \ldots \quad (18)$$

In terms of θ, δ and ρ and a new parameter σ defined by

$$\frac{\alpha_1}{\alpha_2} = 1+\sigma \quad \ldots \quad (19)$$

and neglecting higher order terms we obtain

$$\gamma_{12} = \gamma_{22}\left\{1+\sigma+3\rho+\frac{\delta}{2}-\theta\right\} \quad \ldots \quad (20)$$

The equation (20) is a fair approximation of γ_{12} when the restriction $|\sigma|<0.3$ is obeyed.

With (20), retaining θ and neglecting higher order terms the following simplified expressions for z_p^E is obtained.

$$\frac{g_p^E}{x_xx_2} = \gamma_{22}[h_1(2\sigma+9\rho)+TC_{p1}\{\theta(1+2x_2)-\tfrac{3}{2}\delta\}-\tfrac{1}{4}RT(2\sigma-\theta+\tfrac{3}{2}\delta+9\rho)] \quad \ldots \quad (21)$$

$$\frac{h_p^E}{x_1x_2} = \gamma_{22}\left[(h_1-TC_{p1})(2\sigma+9\rho)+T^2\frac{dC_{p1}}{dT}\{\theta(1+2x_2)-\tfrac{3}{2}\delta\}\right] \quad \ldots \quad (22)$$

$$\frac{v_p^E}{x_1x_2} = -\gamma_{22}\left\{\tfrac{1}{4}v_1+T\frac{dv_1}{dT}\right\}(2\sigma_2-\theta+\tfrac{3}{2}\delta+\tfrac{9}{2}\rho) \quad \ldots \quad (23)$$

In the similar way the contribution z_s^E due to nonspherical shape of the molecules are found out from the perturbations (9). These are

$$\frac{g_s^E}{x_1x_2} = h_1[\Delta_{12}\{1+\theta+(x_1-\tfrac{1}{4})\delta+(\tfrac{1}{4}+3\rho)(x_1-x_2)\}-(\delta_{11}-\delta_{22})$$

$$\{2\theta+(1+x_2)\delta+6\rho\}]+TC_{p1}\delta[\Delta_{12}(x_2-\tfrac{1}{4})+(\delta_{11}-\delta_{22})(\tfrac{1}{2}+x_2)]$$

$$+\tfrac{1}{2}RT[\Delta_{12}\{1+\tfrac{1}{2}\theta+(\tfrac{1}{4}+3\rho)(x_1-x_2)\}-(\delta_{11}-\delta_{22})\{\tfrac{1}{2}\delta+6\rho+\theta(x_1-x_2)\}] \quad \ldots \quad (24)$$

† After correcting a minor error in Anantaraman et al. (1961) for the equation (16) which unfortunately was repeated in Anantaraman et al. (1963). Caused by typographical error in the reprints of the authors.

$$\frac{h_s^E}{x_1x_2} = (2h_1 - TC_{p1} + \tfrac{1}{2}RT)[\Delta_{12}\{1+\theta/2+(\tfrac{1}{4}\delta+3\rho)(x_1-x_2)\} - (\delta_{11}-\delta_{22})\{\tfrac{1}{2}\delta+6\rho+\theta(x_1-x_2)\}] \quad \ldots (25)$$

$$\frac{v_2^E}{x_1x_2} = -\left(\tfrac{1}{2}v_1 + T\frac{dv_1}{dT}\right)\{[\Delta_{12}\{1+\theta/2+\tfrac{1}{4}\delta(x_1-x_2)-\tfrac{3}{4}\rho\} - (\delta_{11}-\delta_{22})\{\tfrac{1}{2}\delta+3\rho(\tfrac{3}{2}-x_2)+\theta(x_1-x_2)\}] + \tfrac{3}{2}T\frac{dv_1}{dT}\delta [\Delta_{12}(x_2-\tfrac{1}{4})+(\delta_{11}-\delta_{22})(x_2+\tfrac{1}{2})] \quad \ldots (26)$$

where $\Delta_{12} = 2(2\delta_{12}-\delta_{11}-\delta_{22})$ and other parameters have been explained elsewhere[1-4]. Δ_{12} and $(\delta_{11}-\delta_{22})$ are very small and can be treated as second order quantities. Hence, if we neglect the product of θ, δ or ρ with either Δ_{12} or $(\delta_{11}-\delta_{22})$ we arrive at the simple form due to Rowlinson. i.e.,

$$\frac{g_s^E}{x_1x_2} = (h_1+\tfrac{1}{2}RT)\Delta_{12} \quad \ldots (27)$$

$$\frac{h_s^E}{x_1x_2} = (2h_1 - TC_{p1} + \tfrac{1}{2}RT)\Delta_{12} \quad \ldots (28)$$

$$\frac{v_s^E}{x_1x_2} = -\left(\frac{1}{2}v_1 + T\frac{dv_1}{dT}\right)\Delta_{12} \quad \ldots (29)$$

It may be pointed out here that out of all the contributions to any excess function z^E only the contributions due to central forces z_0^E are very strongly dependent on θ, δ and ρ. On the other hand z_d^E and z_s^E are little affected by these parameters. For the calculation of z of any system we now encounter two unknown parameters θ and Δ_{12} in the total expression of z^E. We propose to calculate θ and Δ_{12} from the experimental values of two of the excess functions. We choose h^E and v^E for this purpose as these quantities are obtained from direct measurements and consequently are more accurate and reliable. With the values of θ and Δ_{12} thus obtained we would then try to predict g^E to test the consistency of these parameters and hence the proposed theoretical approach.

We have calculated the excess functions of the systems carbon tetrachloride-fluorobenzene, benzene-fluorobenzene and cyclohexane--fluorobenzene systems. The g^E, h^E and v^E of the systems were measured by Anantaraman *et al.* (1963a, b). The results of the calculations have been summarised in Table I. The average values $\bar{z}_0^E$ and $\bar{z}_s^E$ are the averages of the results obtained by taking non-polar and the polar components as reference alternatively.

Anantaraman *et al.* (1963) tried to analyse the results of these systems in light of their modified approach. They predicted the excess functions of the systems cyclohexane-fluorobenzene and benzene-fluorobenzene more or less

TABLE I

Comparison of calculated and experimental excess functions at equimolar composition and 25°C in Cal. or ml. per mole

(a) System : Carbon tetrachloride-fluorobenzene
$\delta = 0.0058$, $\rho = 0.0046$, $\sigma = 0.0324$ $\theta = -0.0138$,
$\Delta_{12} = 0.0159$

Excess function x^E	Calc. z_o^E this work	Calc. z_o^E †	Calc. z_d^E this work	Calc. z_d^E †	Calc. z_s^E this work	Calc. z_p^E this work	Calc. total z_p^E this work	Calc. total z^E †	Expt. z^E
h^E	80.5	4.4	57 3	56.9	−74.3	−2.2	61.0*	61.3*	61.0
v^E	0.25	0.01	0 18	0.19	− 0 33	− 0.02	0.08*	0.20	0.08
g^E	51.7	2.8	23.1	23.0	· 28.5	1.3	45.6	25.8	57.0

(b) System : Benzene-fluorobenzene
$\delta = -0.0065$, $\rho = 0.0268$, $\sigma = 0.0147$, $\theta = 0.0113$
$\Delta_{12} = 0.0003$

h^E	−49.0	−56 0	58 4	58.4	− 1.5	− 5 0	2.1*	2.1*	2.2
v^E	- 0.08	− 0 09	0.18	0.18	− 0.01	− 0.01	0.08*	0 09	0.08
g^E	−31.1	−36.4	22.7	23.0	− 0.6	− 3.6	−12.6	−13.4	0

(c) System : Cyclohexane-fluorobenzene
$\delta = 0.0132$, $\rho = -0.0321$, $\sigma = 0.0688$, $\theta = -0.0250$
$\Delta_{12} = 0.0044$

h^E	173.8	154.5	60.4	60.1	−20.6	3.4	217.0*	214.6*	217.0
v^E	0.65	0.61	0 19	0.18	− 0.10	− 0.02	0.72*	0.79	0.72
g^E	109.6	102.5	24 5	24.6	− 7 8	1.7	128.0	127.1	136.0

* Adjusted to experimental data.
† according to Bhattacharyya, *et al.* (1963a, b).

satisfactorily but their calculated excess functions of the system carbuo-tetrachloride-fluorobenzene was in qualitative agreement only with experimental results. The most interesting feature of this system is that the experimental ratio of g^E: h^E was very nearly unity whereas they found that the calculated excess functions were almost entirely of dipolar origin and thus the system should obey Pople's relation which states that excess functions g_x^E and h^E should bear an approximate relation $g^E : h^E = 1/2$ when they are of pure dipolar origin. The calculated non-polar contributions were rather small owing to the small valnes of δ and ρ of the system (i.e., $\rho = 0.0046$, $\delta = 0.0058$). The value of θ of this

system was also found to be negligible and hence their result did not greatly differ from that obtained by Balescu's theory. These lead to a somewhat paradoxical situation and needs further clarification. So this system has been chosen as a test case for the present approach.

From table 1 it is evident that agreement between the experimental and calculated g^E for the system carbon tetrachloride-fluorobenzene by the present approach is much better and there is a substantial contribution from the structural forces which is of almost equal importance with that of central and dipolar forces. The contribution due to polarisability comes out to be very small in all cases as expected. For the systems benzene-fluorobenzene and cyclohexane-fluorobenzene the contribution due to structural forces are relatively small. This explains the success of Anantaraman *et al.* ( ) to predict their excess functions more or less satisfactorily.

An interesting feature of the theory is that contributions of the structural forces are very similar to those of forces of dipolar origin for h^E and g^E. But though the dipolar effects are always positive for a mixture of non-polar-polar type, the structural effects may be either positive or negative. The $h_s^E : g_s^E$ ratio is also nearly equal to two for the latter. This presents the possibility that the structural forces may cancel or reduce the effect of the dipolar forces so that such a mixture may very well behave as a mixture of non-polar components, But as the $h_s^E : v_s^E$ is not same as that of $h_d^E : v_d^E$ such a simplified assumption may not adequately predict v^E. This explains the $h^E : g^E$ ratio of the system carbon tetrachloride-fluorobenzene and clears up the paradox presented by it. Theory also reveals another fact which should be mentioned. Pople's relation is meant strictly for pure dipolar effects. In an actual mixture of polyatomic molecules, interactions due to different origins remain mixed up. So in the opinion of the author no conclusion as regards the nature of the mixture can be derived simply from a inspection of the observed $h^E : g^E$.

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